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Microwave synthesis of LTN framework zeolite with no organic structure directing agents†

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We present a new microwave synthesis method of Linde Type N zeolite without organic structure directing agents (OSDAs). Linde Type N zeolite (framework type LTN) is one of the most complex zeolite structures with a very large unit cell. It has been synthesised previously using hydrothermal methods. We also report syntheses of zeolite A with LTA framework without OSDAs, by hydrothermal methods at low temperatures (40-60 °C). The as-synthesised zeolites were characterised using X-ray powder diffraction, solid state nuclear magnetic resonance, and scanning electron microscopy. LTA and LTN frameworks are obtained at lower synthesis temperatures, while sodalite (SOD framework) is produced at higher temperatures, confirming the crystalisation of denser zeolites at higher temperatures.

1 Introduction

Zeolites are aluminosilicate materials with meso- or micropores inside their framework structure [1–3]. They have highly crystalline three dimensional frameworks made of SiO_4 or AlO_4 tetrahedral units connected to each other through the oxygen atoms [2,4–7]. The difference in valence between Si and Al atoms is charge balanced by mainly alkali metal cations such as Na^+, Li^+ or K^+.

Zeolites find many industrial uses due to their diverse and highly selective catalytic and ion-exchange properties [8–10]. They are used in petrochemical and fine chemistry as solid-state catalysts, in agriculture for nitrogen fixation in soil, in industry for cleaning radioactive spillages, and for production of washing powders as detergent builders. Most recently they are being investigated for drug delivery in medicine [11].

In this work, we studied three aluminosilicate zeolite frameworks: SOD, LTA and LTN. All of the mentioned frameworks are cubic in symmetry and have similar secondary building units in the framework structure. SOD framework is made of β-cages linked directly via the 4 ring, as can be seen from figure 1a. To make LTA framework, β-cages are connected through D4R, double 4 ring. When eight β-cages are connected by D4R units, a larger α-cage (LTA unit) is formed in the center. LTN framework is more complex and consists of β-cages connected via both D6R units and cancrinite cages,

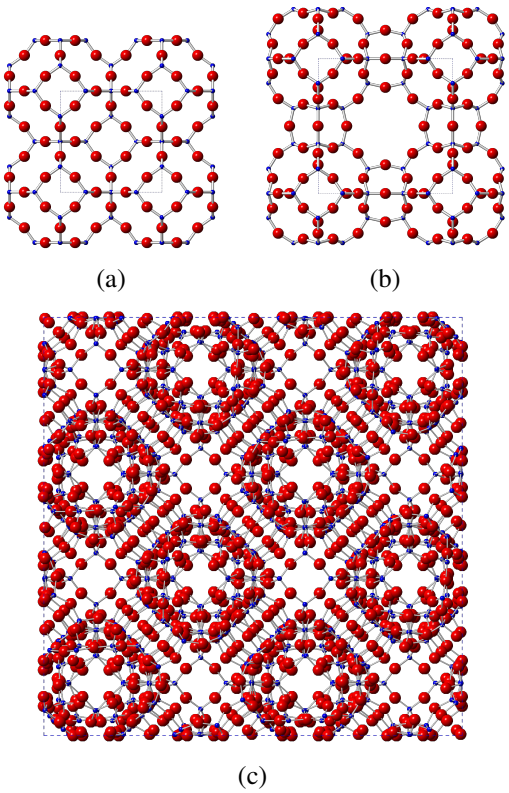

Fig. 1 Three frameworks with β-cage as secondary building unit, viewed along *a*-axis in ball and stick view – (a) SOD (b) LTA and (c) LTN. T atoms are blue, oxygen atoms are red. T–O bonds are displayed. Grey lines show the unit cell in each framework.

† Electronic Supplementary Information (ESI) available: [X-ray powder patterns, solid state NMR spectra and SEM micrographs of as-synthesised zeolite samples]. See DOI: 10.1039/b000000x/

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which leads to the formation of slightly distorted α-cages (figure 1c). This framework has one of the largest unit cells among all known zeolites (a = 35.6Å).

Zeolite with LTA framework has been extensively used for production of washing powders. As the result, both synthesis and properties of zeolite A have been a subject of considerable interest by academics and industry. Sodalite, having relatively small β-cages in its structure, is not a widely used material. It is mainly used as a model for calibration or comparison during measurements on other more complex structures.

Linde Type N zeolite (also know as Z-21) was first synthesized in 1968 by Acara, using tetramethylammonium hydroxide as OSDA[14]. Acara mentioned in this patent that this zeolite adsorbs water preferentially over nitrogen or oxygen, thus suggesting its usefulness as a desiccant for oxygen or nitrogen streams. In 1971, Duecker et al. synthesised this zeolite hydrothermally without using OSDAs[13]. In 1982, Falth and Andersson solved the crystal structure of Linde Type N zeolite[15], and in 1983 Shepelev et al. reported a crystal structure for Na Z-21 zeolite which has a LTN framework topology. While zeolite A and sodalite have been studied extensively in the last 50 years, there are fewer studies on Linde Type N zeolite. Here for the first time, we report a synthesis of Linde Type N zeolite with no OSDAs using a microwave method.

2 Experimental

Here we describe recipes for synthesis of all zeolites in this study. The synthesis method for zeolite A without OSDAs and sodalite were modified from Smaihi et al.[12]. The microwave synthesis of Linde Type N zeolite described here is new. We also repeated the hydrothermal synthesis of Linde Type N zeolite following the method described by Duecker et al.[13] The summary of the recipes is presented in table 1.

2.1 Hydrothermal synthesis of zeolite A without OSDA

Zeolite A with gel composition Al_2O_3 : $2SiO_2$: $15Na_2O$: $400H_2O$ was prepared as follow. 6.78g of sodium hydroxide (Fisher) was dissolved in 40 cm^3 of deionized water and divided into two 20 cm^3 portions. 0.988g of sodium aluminate was added to one portion while 2.42g of colloidal silica (Ludox HS-30, 30wt% SiO_2, Aldrich) was added to the other. Both $Al_2O_3/Na_2O/H_2O$ solution and silica solution was stirred for 90 minutes at room temperature. The silica solution was then added to the $Al_2O_3/Na_2O/H_2O$ solution in a 60ml polypropylene bottle, and stirred for 15 minutes. The homogeneous gel was sealed and treated hydrothermally at various temperature and time, e.g. 40°C, 50°C, 60°C, 70°C, 80°C, 95°C for 24 hours, and 95°C for 48 hours. Each sample was washed with distilled water until pH 7 was attained, and dried in an oven at 110°C.

2.2 Microwave synthesis of Linde Type N zeolite without OSDA

Linde Type N zeolite was synthesised using 12.9g colloidal silica (Ludox HS-30, 30wt% SiO_2, Aldrich), 10.1g sodium aluminate (Al_2O_3 50-56%, Na_2O 40-45%, Sigma -Aldrich), 106.6g of sodium hydroxide (analytical reagent grade, 98.86%, Sigma -Aldrich) and 200ml of deionized water. Sodium hydroxide was dissolved in deionized water until a clear solution was formed. The alkaline solution was divided into two equal volumes, e.g. 100ml. Colloidal silica and sodium aluminate was then added seperately to each portion. The $Al_2O_3/Na_2O/H_2O$ solution and silica solution were stirred for 24 hours at room temperature to ensure the solution has been thoroughly mixed. The silica solution was then added to the $Al_2O_3/Na_2O/H_2O$ solution, and stirred for 1 hour at room temperature. 40 ml of the resulting gel was loaded into an 'easy prep plus' vessel of Mars 6 microwave. The following conditions were used during synthesis: 40°C, 60°C, 80°C, 90°C, 100°C, 120°C for 1 hour. Two more experiments were repeated using fumed silica (Aldrich) at 60°C and 90°C for 1 hour. All of the above reactions once completed were filtered using a Buckner funnel and washed with deionized water. Once filtered, the samples were dried in an oven for 48 hours at 60°C.

2.3 Hydrothermal synthesis of Linde Type N zeolite without OSDA

The method is based on the patent described by Duecker et al.[13] 10g of sodium hydroxide was dissolved in 25ml of deionized water followed by 0.95g of aluminium hydroxide and stirred at 95°C for 1 hour until a clear solution is formed. 2.18ml of sodium silicate solution was then added and shaked vigorously for 1 minute. The resulting gel was transfered into a 60ml polypropylene bottles and heated at 100°C for 1 hour, then washed with distilled water until pH 7 was attained, and dried in an oven at 100°C overnight.

3 Characterization

3.1 X-ray powder diffraction (XRPD)

The powder patterns of zeolite A were obtained using a Philips X'pert X-ray diffractometer or a Philips PW1792 X-ray diffractometer both operating with Cu Kα radiation. The powder patterns of LTN zeolites were measured using a D8 powder diffractometer using Cu Kα radiation.

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Table 1 Summary of recipes for synthesis of zeolite A and Linde Type N zeolite

Method	Zeolite	Framework	Reagents	Synthesis method	Time/Hr(s)	Ref.
1	Zeolite A	LTA	Ludox HS-30 (30wt% SiO_2), sodium aluminate, sodium hydroxide	Hydrothermal	24	modified from Smaihi et al.[12]
2	Linde Type N	LTN	Ludox HS-30 (30wt% SiO_2), sodium aluminate, sodium hydroxide	Microwave	1	this study, new method
3	Linde Type N	LTN	sodium silicate solution, aluminium hydroxide, sodium hydroxide	Hydrothermal	1	Duecker et al.[13]

3.2 Solid state magic angle spinning nuclear magnetic resonance (SS MAS NMR)

^{29}Si, ^{27}Al and ^{23}Na NMR spectra were measured using a VARIAN VNMRS 400 spectrometer using direct excitation (DE) method, with neat tetramethylsilane, 1M aqueous aluminium nitrate, and 1M aqueous sodium chloride solution as reference respectively. The spinning rate of ^{29}Si NMR was 6.8 kHz, ^{27}Al and ^{23}Na NMR were 14kHz. Solid-state NMR spectra were obtained at the EPSRC UK National Solid-state NMR Service at Durham.

3.3 Scanning electron microscopy (SEM)

SEM images were obtained from a Hitachi S-4300 scanning electron microscope. The powder samples for SEM were coated with platinum metal of 5nm thickness.

4 Result and Discussion

4.1 X-ray powder diffraction

The powder patterns of as-synthesised zeolite A with no OSDA at various temperatures are shown in figure 2. Pure phase of zeolite A was formed when treated hydrothermally for 24 hours at 40 °C, 50 °C and 60 °C[16]. When the temperature was increased to 70 °C, a mix of zeolite A and sodalite was observed. The sodalite 110 peak can clearly be seen around 14 °2θ. The amount of sodalite in the as-synthesised sample increases from 70 °C to 95 °C. The sample synthesised at 95 °C for 24 hours consisted mostly of sodalite. When we increased the reaction time from 24 hours to 48 hours at 95 °C, single phase sodalite was synthesised. Our data show that zeolite A can be synthesised at temperature as low as 40 °C without OSDA.

The transformation from LTA framework to SOD framework with increased temperature has been observed previously[17–21]. Sodalite is a denser zeolite (framework density 16.7T/nm^3) compared to zeolite A (framework density 14.7T/nm^3), so it is reasonable to expect that it will preferentially form with increased temperature[17–21]. Increasing the duration of hydrothermal treatment also favors the formation of sodalite at high temperature.

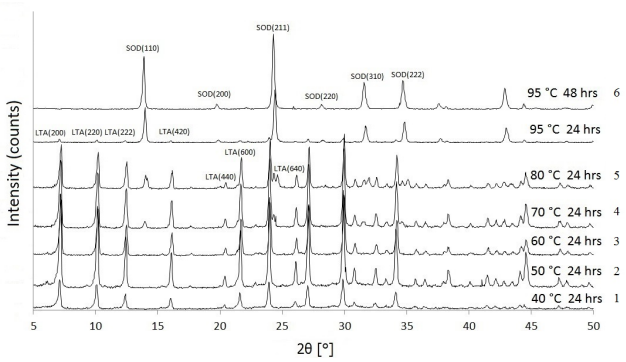

Fig. 2 Powder patterns of as-synthesised zeolite A and sodalite without OSDA under hydrothermal conditions. Zeolite A is formed at temperature between 40 °C and 80 °C, while sodalite is formed above 70 °C

We then decided to reproduce these results using a microwave method[22,23] instead of standard hydrothermal treatments. We attempted to synthesise zeolite A with no OSDA using a microwave with the same batch composition, and Linde Type N zeolite was formed. The powder pattern of as-synthesised zeolite samples using microwave synthesis was shown in figure 3. No crystalline phase was observed at 40 °C. Linde Type N zeolite was synthesised between 60 °C and 90 °C(figure 3a). Sodalite was formed at temperature above 100 °C (figure 3b). Change of silica source did not affect the formation of Linde Type N between 60 °C and 90 °C†. LTN framework with density 17T/nm^3 is comparable with SOD framework with framework density 16.7T/nm^3.

We also repeated the hydrothermal synthesis of Linde Type N zeolite in the patent published by Duecker et al.[13] Figure 4 shows the powder pattern of the as-synthesized Linde Type N zeolite at 100 °C and the corresponding simulated pattern.

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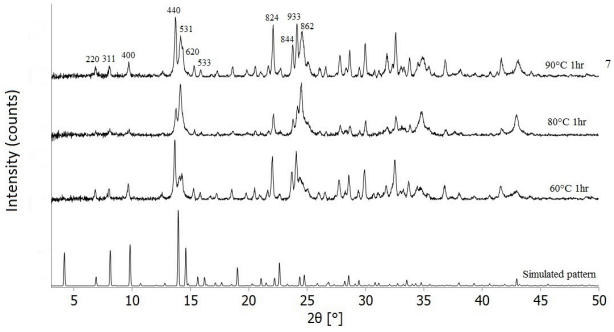
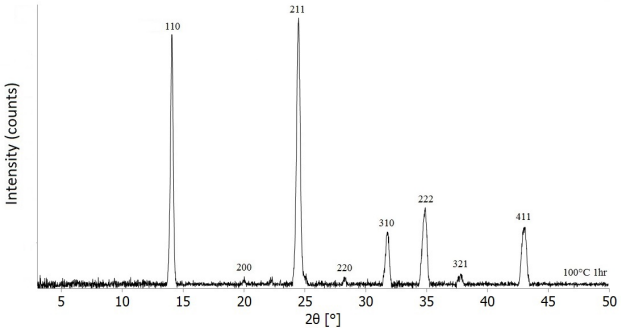
Table 2 SS MAS MNR of as-synthesised zeolite samples

Sample	Phase	Temp / °C	Time / hour(s)	Si / ppm	Al / ppm	Na / ppm	Method
1	Zeolite A	40	24	-84.9, -89.5	58.6	-2.4	Hydrothermal, no OSDA
2	Zeolite A	50	24	-84.5, -85.4, -86.5, -89.3	58.8	-1.9	Hydrothermal, no OSDA
3	Zeolite A	60	24	-86.5, -89.4, -91.1	58.6	-3.4	Hydrothermal, no SDAs
4	Zeolite A, Sodalite	70	24	-83.5, -86.6, -89.4, -94.6	58.5	-3.1	Hydrothermal, no OSDA
5	Zeolite A, Sodalite	80	24	-83.5, -86.5, -89.3	58.5	-3.1	Hydrothermal, no OSDA
6	Sodalite	95	48	-80.9, -83.8, -85.2	63.7, 65.3	4.0, -4.1	Hydrothermal, no OSDA
7	Linde Type N	90	1	-83.7, -85.3, -86.3	60.6, 63.5	2.0, -4.8	Microwave, no OSDA



(a)



(b)

Fig. 3 Powder patterns of as-synthesised sodalite and Linde Type N zeolite without OSDAs using microwave methods. (a) Linde Type N zeolite forms above 60 °C (b) Sodalite forms at and above 100 °C

The synthesis was also repeated at 60 °C for 1 hour with no formation of any amorphous or crystallized phase. Compare to this hydrothermal method, using the microwave method we can synthesise Linde Type N zeolite at lower temperature.

4.2 Solid State Magic Angle Spinning Nuclear Magnetic Resonance (SS MAS NMR)

We employed Solid State MAS NMR[24,25] to study the zeolite A/sodalite synthesised hydrothermally and Linde Type N

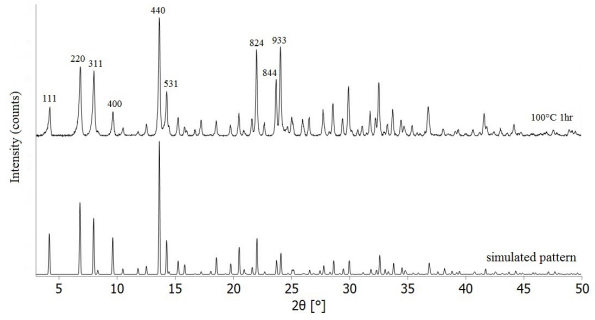


Fig. 4 Powder patterns of as-synthesised Linde Type N zeolite without OSDA using hydrothermal method

synthesised using the microwave method. Table 2 summarises the NMR data collected from zeolite samples synthesised using various methods with different reaction temperatures and times.

Variation in spectra were observed when we synthesised zeolite A without OSDA (Table 2, sample 1-6). Since some of the zeolites were synthesised at temperature as low as 40 °C, we expected to see silanol signals on NMR spectra. The presence of silanol species in zeolite samples was confirmed by using ^{29}Si cross-polarization (CP) MAS NMR†.

It is interesting to see that there is one signal around -89.4ppm which presents in all samples with zeolite A (Table 2, sample 1-5). This might indicate that it is an intrinsic signal for the LTA framework[26]. This peak is usually attributed to Si(4Al) species in zeolites[3].

Linde Type N zeolite synthesised using microwave method without OSDA (Table 2, sample 7) showed a relatively simple spectrum. Only two major local Si environments were observed at -85.3ppm and -86.3ppm (silanol species at -83.7ppm).

^{27}Al and ^{23}Na MAS NMR spectra of zeolite samples synthesised hydrothermally with no OSDA at 40 °C, 50 °C, 60 °C, 70 °C and 80 °C (Table 2, sample 1-5) show only one Al and one Na local environment respectively. This indicates that Al were tetrahedrally coordinated in the framework associated

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with Na ions. Sodalite (Table 2, sample 6) and Linde Type N zeolite (Table 2, sample 7), however, showed an extra broad signal. Although this signal is also tetrahedral framework Al, we were not be able to explain such broadening.

For single phase zeolites, we were able to calculate the Si/Al ratio by using equation (1)[27–30]. Table 3 shows the Si/Al ratio of selected as-synthesised zeolite samples. For zeolite sample synthesised hydrothermally with no OSDA at 50 °C and 95 °C, the estimated ratio was 1.4 and 1.2 respectively. The estimated Si/Al ratio of the Linde Type N zeolite was 1.1.

$$\left(\frac{Si}{Al}\right)_{framework} = \frac{\left(\sum_{n=0}^{4} I_{Si(nAl)}\right)}{\left(\sum_{n=0}^{4} 0.25 n I_{Si(nAl)}\right)} \quad (1)$$

where $I_{Si(nAl)}$ is the relative intensity of the $Si(OAl)_n(OSi)_{4-n}$.

Table 3 Si/Al ratio of single phase as-synthesised zeolite

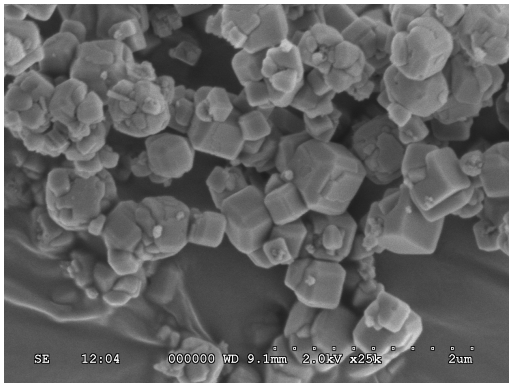
Sample	Phase	Si/Al ratio
1b	Zeolite A	1.4
1e	Sodalite	1.2
2	Linde Type N	1.1

The suggested Si/Al ratio for zeolite A with no OSDA, and for sodalite, is 1[31,32]. The as-synthesised zeolite A with no OSDA had a slightly higher Si/Al ratio, while as-synthesised sodalite is close to the suggested value.

4.3 Scanning Electronic Microscopy (SEM)

The SEM micrographs of selected as-synthesized zeolite samples are shown in Figure 5, 6. When we synthesise zeolite A hydrothermally with no OSDA at different temperatures, we saw the change of morphology from the formation of zeolite A at low temperature to sodalite at high temperature. Although the powder pattern of the zeolite sample synthesised at 50 °C showed a single phase, aggregates of small crystals less than 0.2 μm without defined shape were observed†. At temperatures of 70 °C (figure 5(a)) and 80 °C†, we saw a mixture of cubic zeolite A crystals, as well as sodalite crystals with undefined shape. Sodalite crystals with hexagonal faces formed at 95 °C, with average size of 1 μm as shown in figure 5(b).

Figure 6 shows the zeolite samples synthesised using microwave method without using OSDA. Linde Type N zeolite crystals with various morphology at different temperatures were observed. At 60 °C, Linde Type N zeolite formed as truncated cubes associated with spheres with rough surface (figure 6(a)). The truncated cubic crystals grow into aggregates and eventually to 2 μm spheres with smooth surface at 90 °C†. Uniform sodalite crystal with size 3μm were observed when the temperature increased above 100 °C, as shown in figure 6(b).



(a)

(b)

Fig. 5 SEM micrographs of zeolite samples synthesised hydrothermally with no OSDAs at different temperatures (a) Mix of zeolite A and sodalite at 70 °C (b) Sodalite at 95 °C

5 Conclusions

Linde Type N zeolite, with an LTN framework, has been synthesized without structure directing agents at 60 °C in an hour using a microwave method. This is a lower temperature synthesis compared to the hydrothermal method described by Duecker et al.[13] This zeolite has a very complex structure and is considered as one of the most complex zeolites among the 216 known today.

We found that both zeolite A and Linde Type N zeolite can be crystallized at relatively low temperatures (40–50 °C) in pure form. At higher temperatures, competing sodalite phase appears during the crystallization. However, when synthesising Linde Type N zeolite hydrothermally, no sodalite phase is observed at 100 °C. We also studied some of the as-synthesised zeolites using Solid State MAS NMR and SEM. NMR helped us to determine the Si/Al ratios of the as-synthesised zeolites and we attempted to rationalize their chemical shifts. SEM helped us to see their crystal morphology and size.

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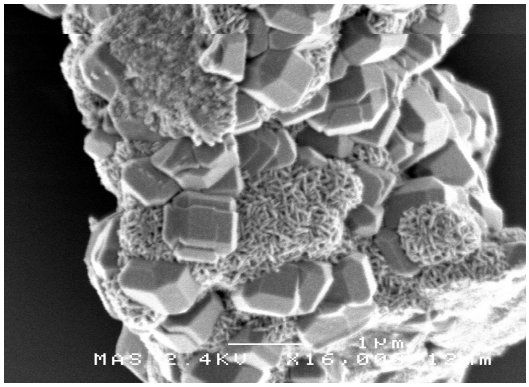
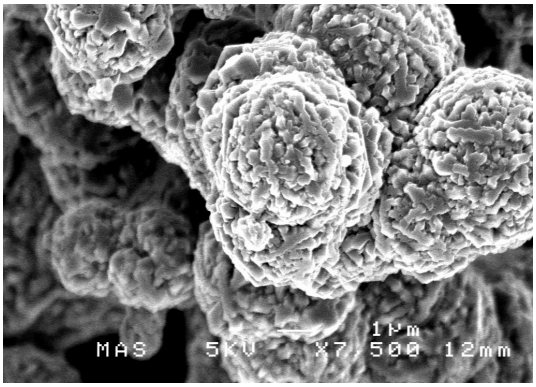


(a)



(b)

Fig. 6 SEM micrographs of as-synthesised zeolite samples using microwave method with no OSDA at different temperatures (a) Linde Type N zeolite at 60 °C (b) Sodalite at 100 °C

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